

Band-Filling Control of π - d Electron System Based on Bis(ethylenedithio)tetrathiafulvalene Cation Radical Salts

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Now, many organic conductors as well as Mott insulators based on radical cation or anion salts have been obtained.¹ It is, however, usually difficult to control further the filling of the conduction electron band or the effective valence because of extreme sensitivity of the crystal structure to substituents or interstitial dopants. In other words, a modification of counter-anions or cations usually results in a change of crystal structure which does not enable one to investigate the physical properties of the salt systematically. Nevertheless, chemical control of band filling may be effective for obtaining molecular conductors as in many doped Mott insulators such as high- T_c cuprate superconductors.² To control the band filling in a conducting system which consists of donor π molecules, an alloyed-anion system containing two kinds of negative charge is needed. With this background in mind, we adopted a mixture of tetrachlorometalate (MCl_4^{n-}) as counteranions of BEDT-TTF (ET, BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) radical cation salts $((ET)_y[(MCl_4^{2-})_{1-x}(M'Cl_4^{-})_x])$, $M^{2+} = Mn^{2+}$ or Zn^{2+} , $M'^{3+} = Fe^{3+}$ or Ga^{3+}) to realize a carrier-doped magnetic molecular system. Crystals of TTF derivatives with magnetic tetrahalogenometalate counteranions are of current interest since the family is producing novel magnetic molecular conductors,³ and the present system is one such example. The valence of tetrachlorometalate depends on a valence of positively charged central metal (M). Monovalent anions (e.g., $GaCl_4^-$ and $FeCl_4^-$) and divalent anions (e.g., $ZnCl_4^{2-}$ and $MnCl_4^{2-}$) are of the almost same size, being favorable for making an alloy system. In addition, since the metals are wrapped by chlorine atoms, randomness due to the difference of valence can be smaller than in the case of an uncovered metal cation.

Single crystals of cation radical salts were prepared by the electrocrystallization and obtained as very fine brownish-black needles. The ratio of $M:M'$ in each batch was estimated by using inductively coupled plasma mass spectrometry (ICP),⁴ and the cell parameters of each crystal were determined by X-ray crystallographic analysis with the use of an image plate (IP) system. The crystal structure of the end material, $((ET)_yMnCl_4)$

[ref 5] is different from the known structure of ET cation radical salt with divalent metalate MCl_4^{2-} $((ET)_3(MCl_4)_2$, $M = Mn, Zn$)⁶ but appears rather similar to the monovalent salt $((ET)_2(MCl_4)$, $M = Fe, Ga$),⁷ although the ratio of donor to anion is estimated to be $y \approx 3.6$ by the elemental analysis and ICP analysis.⁸ On the basis of the value of $y = 3.6$, a valence of ET is estimated to be +0.56. Thus, the filling of the ET π band is perhaps close to $3/4$ and likely causes the Mott-insulating state in the dimerized lattice. The cell parameters of the Fe-doped crystal $((ET)_y - [(MnCl_4)_{1-x}(FeCl_4)_x])$, $x \approx 0.05$ (batch) was resolved as follows: $a = 34.33 \text{ \AA}$, $b = 14.47 \text{ \AA}$, $c = 6.68 \text{ \AA}$, $\alpha = \beta = \gamma = 90.00^\circ$. For the Fe-doped crystal (e.g., $x = 0.06$), the change of the band filling or the ET molecular valence is about 0.02. By consideration of the cell parameters, the crystal structure of Fe-doped salt is assigned as being almost identical with that of Mn-pure salt. From the Patterson method analysis of the X-ray diffraction data of the Fe-doped crystal, we can predict that ET cation radicals are aligned along the b axis with columnar structure as shown in the inset of Figure 1.⁹ Anions are expected to be located between donor columns. Furthermore, the cell constants of Zn-pure salt $((ET)_y(ZnCl_4))$ and Ga-doped salt $((ET)_y[(ZnCl_4)_{1-x}(GaCl_4)_x])$, $x = 0.04$ were determined to be nearly the same as those of Mn-pure or Fe-doped salt. Thus, all the neat and alloyed systems, $(ET)_y[(MnCl_4^{2-})_{1-x}(FeCl_4^{-})_x]$, and $(ET)_y[(ZnCl_4^{2-})_{1-x}(GaCl_4^{-})_x]$, investigated in this study form the isostructural family. The two tested series of mixed crystals, $(ET)_y[(MnCl_4^{2-})_{1-x}(FeCl_4^{-})_x]$ and $(ET)_y[(ZnCl_4^{2-})_{1-x}(GaCl_4^{-})_x]$, are respectively characterized by magnetic ($S(Mn^{2+}) = S(Fe^{3+}) = 5/2$) and nonmagnetic ($S(Zn^{2+}) = S(Ga^{3+}) = 0$) anions.

The temperature dependence of resistivity measured along the stacking axis (b axis) is shown in Figure 1 for those neat and alloyed anion compounds. The crystal which includes only divalent anions, Zn-pure salt $((ET)_y(ZnCl_4))$, shows insulating behavior with ρ_{rt} (room temperature resistivity) = 10–50 Ωcm and E_a (activation energy) = 0.037 eV. However, once a slight amount of monovalent $GaCl_4^-$ is doped to the crystal as in a form of $(ET)_y[(ZnCl_4)_{1-x}(GaCl_4)_x]$, the crystal shows low resistivity such as $\rho_{rt} = 0.1 \Omega\text{cm}$ and metallic behavior around room temperature as shown in Figure 1a. From measurements of the magnetic susceptibility of the Ga-doped salts, it was found that the salt has constant positive susceptibility ($\chi = 9 \times 10^{-4} \text{ emu}\cdot\text{mol}^{-1}$) between room temperature and 100 K (Figure 2), being reminiscent of Pauli paramagnetism. The crystals of Fe-doped salts, $(ET)_y[(MnCl_4)_{1-x}(FeCl_4)_x]$, also have low resistivity ($\rho_{rt} = 5\text{--}0.02 \Omega\text{cm}$), and some crystals remain metallic down to 4.2 K, while the parent (undoped) crystal of $(ET)_yMnCl_4$ shows insulating behavior with $\rho_{rt} = 15 \Omega\text{cm}$ and $E_a = 0.037 \text{ eV}$ (Figure 1b). The crystals of Ga-doped and Fe-doped salts thus show drastic reduction of the resistivity as compared with those of Zn-pure

(4) There are some scatter ($\Delta x < 0.005$) for each crystal in a batch. Galvanostatic electrocrystallization of ET was performed in acetonitrile using Pt electrodes in the presence of a mixture of $(Et_4N)_2MCl_4$ and $Et_4NM'Cl_4$ as a supporting electrolyte. The ratio of $M:M'$ of obtained single crystals was not equal to that of the electrolyte. Actual dopant ($M'Cl_4$) concentration in the dopant crystal, which was determined by the ICP analysis, monotonically increased with the quantity of loaded $Et_4NM'Cl_4$.

(5) Crystal data: $a = 33.12 \text{ \AA}$, $b = 14.75 \text{ \AA}$, $c = 6.74 \text{ \AA}$, $\alpha = \beta = \gamma = 90.00^\circ$.

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(8) Anal. Calcd for $C_{180}H_{174}C_{20}Mn_5O_{15}S_{144}$ $((ET)_y(MnCl_4)(H_2O)_z$, $y = 3.6$, $z = 3$): C 26.43, H 2.14, S 56.46; found: C 26.37, H 2.22, S 56.50. Some water molecules seem to be included in a crystal. From a ratio of S:Mn by ICP analysis, $y \approx 3.5$ was obtained.

(9) A donor stacking pattern (ca. $8 \text{ \AA} = \text{ET stacking} \times 2$) was observed by an STM measurement.

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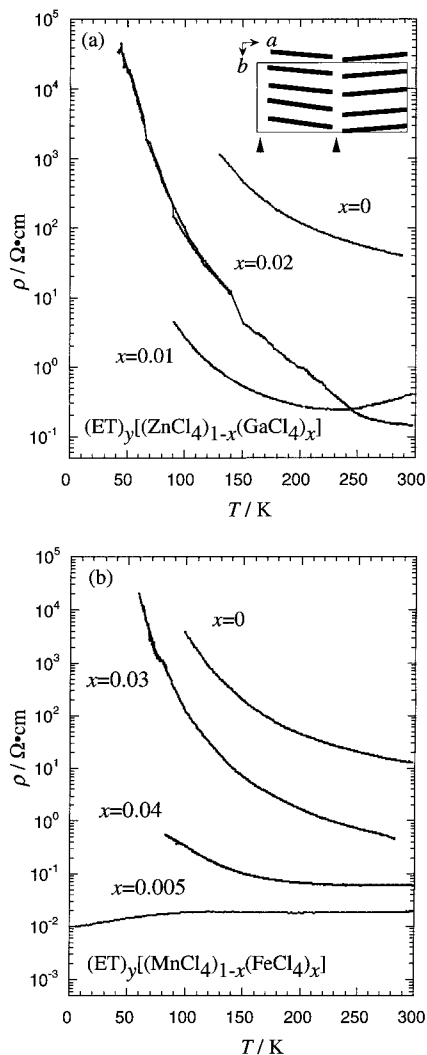


Figure 1. (a) Temperature dependence of the resistivity for $(\text{ET})_y[(\text{ZnCl}_4)_{1-x}(\text{GaCl}_4)_x]$. The inset depicts a schematic crystal structure judged from the X-ray diffraction data. (b) Temperature dependence of the resistivity for $(\text{ET})_y[(\text{MnCl}_4)_{1-x}(\text{FeCl}_4)_x]$. The measurements were done by a four-probe method.

and Mn-pure salts, perhaps owing to a small amount (0.005–0.04 in molar fraction) of monovalent anions as dopants. In the case of the κ' -(BEDT-TTF) $_2\text{Cu}_2(\text{CN})_3$ crystal, it is suggested that a superconductivity is realized by carrier doping into the Mott insulator that arises from minute disproportionation of the valence of the Cu ion ($\text{Cu}^+/\text{Cu}^{2+}$).¹⁰ Such band filling control is likely realized also in the present alloyed-anion systems and drives the insulator to metal transition.

The temperature dependence of the magnetic susceptibility of the Mn–Fe system (Figure 2) was unconventional as magnetic molecular solids. The χT vs T curve of the Mn-pure crystal obeys the Curie–Weiss law, indicating the presence of $S = 5/2$ local spins with weak antiferromagnetic interaction (Weiss temperature $\theta = -3$ K). By contrast, the curve for the Fe-doped salt crystals can be viewed as the overlap of the Curie–Weiss and Pauli-like (temperature-independent) paramagnetism. For example, the curve of the batch where $x = 0.03$ (curve *a* in Figure 2) can be represented by the parameters, C (Curie constant) = 3.35 $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = +2$ K, and temperature independent susceptibility $\chi_{\text{Pauli}} = 6.5 \times 10^{-3}$ $\text{emu}\cdot\text{mol}^{-1}$. The values of C and χ_{Pauli} depend on the sample batches, but in all cases, the C values are smaller than the value (4.375 $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$) expected for the

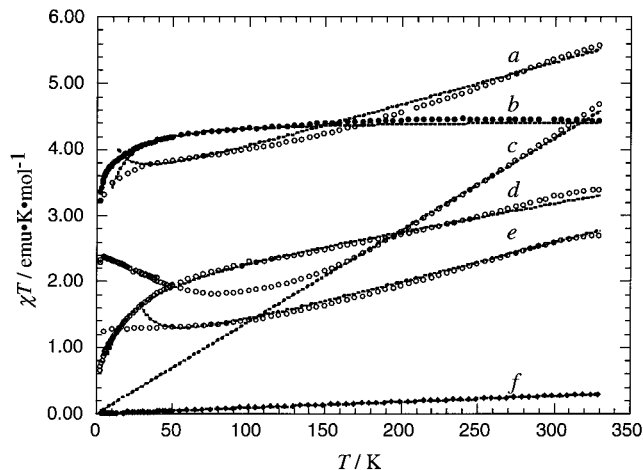
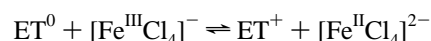
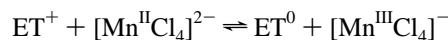


Figure 2. The χT vs T plot of $(\text{ET})_y[(\text{MCl}_4)_{1-x}(\text{M}'\text{Cl}_4)_x]$. The experimental data are represented by open circles ($(\text{ET})_y[(\text{MnCl}_4)_{1-x}(\text{FeCl}_4)_x]$), solid circles ($(\text{ET})_y[(\text{ZnCl}_4)_{1-x}(\text{GaCl}_4)_x]$), and solid squares ($(\text{ET})_y[(\text{ZnCl}_4)_{1-x}(\text{GaCl}_4)_x]$). The calculated curves using the formula, $\chi = C/T - \theta + \chi_{\text{Pauli}}$ are depicted by broken lines. The parameters for the calculations are as follows: (a) $(\text{ET})_y[(\text{MnCl}_4)_{1-x}(\text{FeCl}_4)_x]$ ($x = 0.03$); $C = 3.35$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = 2$ K, $\chi_{\text{Pauli}} = 6.5 \times 10^{-3}$ $\text{emu}\cdot\text{mol}^{-1}$. (b) $(\text{ET})_y[(\text{MnCl}_4)]$ (Mn-pure); $C = 4.45$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = -3$ K; (c) $(\text{ET})_y[(\text{MnCl}_4)_{1-x}(\text{FeCl}_4)_x]$ ($x = 0.005$); $C = 0$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = 0$ K, $\chi_{\text{Pauli}} = 1.4 \times 10^{-2}$ $\text{emu}\cdot\text{mol}^{-1}$. (d) $(\text{ET})_y[(\text{MnCl}_4)_{1-x}(\text{FeCl}_4)_x]$ ($x = 0.06$); $C = 2.05$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = -10$ K, $\chi_{\text{Pauli}} = 4.0 \times 10^{-3}$ $\text{emu}\cdot\text{mol}^{-1}$. (e) $(\text{ET})_y[(\text{MnCl}_4)_{1-x}(\text{FeCl}_4)_x]$ ($x = 0.04$); $C = 0.7$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = 15$ K, $\chi_{\text{Pauli}} = 6.2 \times 10^{-3}$ $\text{emu}\cdot\text{mol}^{-1}$. (f) $(\text{ET})_y[(\text{ZnCl}_4)_{1-x}(\text{GaCl}_4)_x]$ ($x = 0.02$); $C = 0$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = 0$ K, $\chi_{\text{Pauli}} = 9 \times 10^{-4}$ $\text{emu}\cdot\text{mol}^{-1}$.

localized spin on $\text{Mn}^{2+}/\text{Fe}^{3+}$ ($S = 5/2$). In addition, the χ_{Pauli} values are always larger than the ordinary metallic ET cation radical salt.¹¹ Further, in the case of the batch where $x = 0.005$ (metallic down to 4.2 K, curve *c* in Figure 2), there seems to be no Curie term at the temperatures between 150 and 330 K, and in the low-temperature region, the χT value increases with decreasing temperatures. Judging from the reduced C value and enhanced χ_{Pauli} value, we can expect that the d -electrons on the anion do not behave with completely localized spins but participate in composing the states near the Fermi level as well as the ET π electrons.¹² This suggests also the partial electron transfer between donor and anion in the doped crystal. The electron transfer may be explained by a consideration of the near valence degeneracy of tetrachlorometalate ions such as



Such a mixed valence nature indicates, in turn, the strong coupling between donors (π) and anions (d) in the crystal. Thus, the band filling control in the ET system with magnetic counteranions gives rise to a novel metallic conduction band which is composed not only of π -electron but also of d -electron states.

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